57Fe Mössbauer spectra from fluorinated phases of Fe0.50M0.50(M = Co,Mg)Sb2O4

Berry, Frank J.; De Laune, Benjamin P.; Greaves, Colin; Thomas, Michael F.; Jumas, Jean-claude

DOI:
10.1007/s10751-019-1621-8

Hyperfine Interactions (2019) 240:77
https://doi.org/10.1007/s10751-019-1621-8

^{57}Fe Mössbauer spectra from fluorinated phases of $Fe_{0.50}M_{0.50}$(M = Co,Mg)Sb_2O_4

Frank J. Berry[1] · Benjamin P. de Laune[1] · Colin Greaves[1] · Michael F. Thomas[2] · Jean-Claude Jumas[3]

Published online: 27 June 2019

Abstract
Fluorinated phases formed by reaction of $Fe_{0.5}Co_{0.5}Sb_2O_4$ and $Fe_{0.5}Mg_{0.5}Sb_2O_4$ with gaseous fluorine have been examined by ^{57} Fe Mössbauer spectroscopy between 298 and 5 K. The degree of oxidation of $Fe^{2+}$to Fe^{3+}has been used to quantify the amount of fluorine incorporated within the channels of the schafarzikite-related structure and enable the evaluation of the compositions as $Fe_{0.5}Co_{0.5}Sb_2O_4F_{0.41}$ and $Fe_{0.5}Mg_{0.5}Sb_2O_4F_{0.31.}$ The multiplicity of components observed in the spectra recorded in the paramagnetic regime can be related to the number of near neighbour fluoride ions which lie in the channels at the same value of the crystal *z*-coordinate as the iron ions. Comparison of the magnetically ordered spectra recorded at lower temperatures from $Co_{0.5}Fe_{0.5}Sb_2O_4F_{0.41}$ with those recorded previously from $FeSb_2O_4$ indicates that the insertion of fluoride ions into the channels of the structure does not affect the angle between the EFG and magnetic hyperfine field.

Keywords Schafarzikite · Fluorinated oxides · Mössbauer spectroscopy

1 Introduction

The insertion of fluorine into two-dimensional structures induces structural changes and electronic properties resulting from the oxidation of metal ions in the host material. The conversion of semiconducting La_2CuO_4 to superconducting $La_2CuO_4F_x$ [1] illustrates this type of reaction and other examples are documented in a recent review [2]. As a part of our

This article is part of the Topical Collection on *Proceedings of the 5th Mediterranean Conference on the Applications of the Mössbauer Effect (MECAME 2019) and 41st Workshop of the French-speaking Group of Mössbauer Spectroscopy (GFSM 2019), Montpellier, France, 19-23 May 2019*
Edited by Pierre-Emmanuel Lippens, Yann Garcia, Moulay-Tahar Sougrati and Mira Ristic (†)

✉ Frank J. Berry
f.j.berry.1@bham.ac.uk

[1] School of Chemistry, The University of Birmingham, Birmingham B15 2TT, UK

[2] Department of Physics, University of Liverpool, Liverpool L69 3BX, UK

[3] Institut Charles Gerhard (UMR 5253), Universite Montpellier, Case Courrier 1502, Place Eugene Bataillon, 34095 Montpellier Cedex 5, France

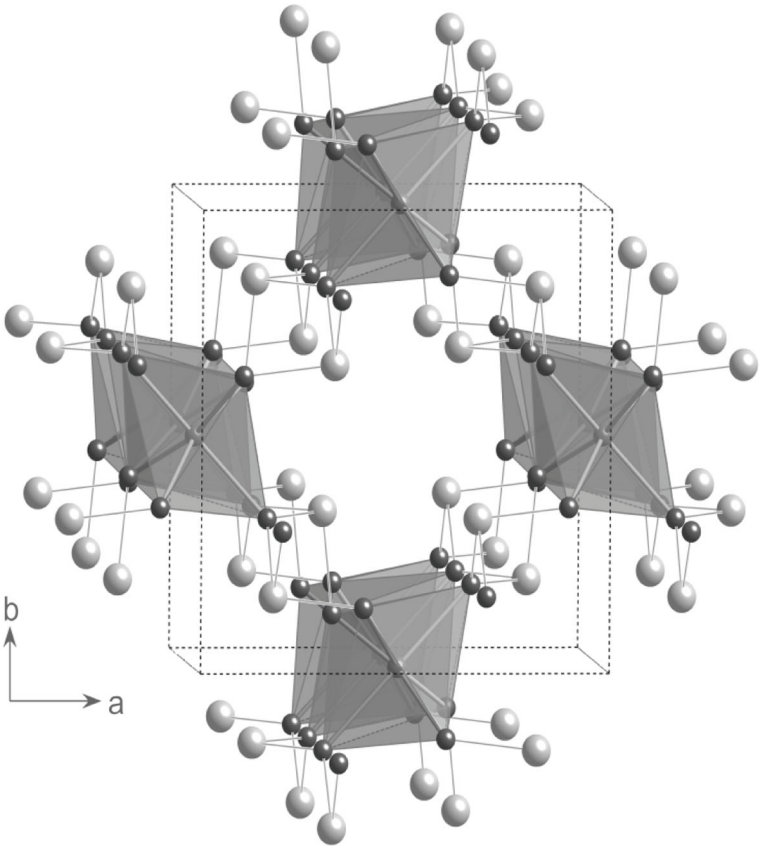

Fig. 1 The structure of $FeSb_2O_4$: FeO_6 octahedra are shaded with Fe^{2+} ions located within the octahedra; O^{2-} ions are shown as black spheres and Sb^{3+} ions are shown as white spheres

ongoing interest in the fluorination of inorganic structures we have recently reported on the accommodation of fluorine within the narrow one-dimensional channels of phases related to the mineral schafarzikite of composition $FeSb_2O_4$ [3].

The compound $FeSb_2O_4$ is isostructural with the tetragonal form of Pb_3O_4 [4, 5](Fig. 1) and consists of rutile-related chains of FeO_6 octahedra along the *c*-axis linked by trigonal pyramidal Sb^{3+} cations which, being bound to three oxygen anions, possess a lone pair of electrons which can be regarded as a fourth ligand. The Fe-Fe distance within the chains (2.96 Å) is shorter than the nearest Fe-Fe distance within the layers (6.07 Å) and is consistent with the one-dimensional character of $FeSb_2O_4$. The material undergoes an antiferromagnetic transition around 45 K [6, 7]. The ^{57}Fe Mössbauer spectrum of $FeSb_2O_4$ at ca. 4.2 K is unusual, being the result of combined magnetic hyperfine and electric quadrupole interactions of comparable strength [8–10] and, together with data recorded above T_N [11], has been used to determine the order of the t_{2g} orbital energy levels. The literature also documents some structurally related compounds of composition MSb_2O_4 (M = Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Mg^{2+}) [12–17].

We have also prepared new phases involving substitution on the M site. The magnetic properties deduced from neutron diffraction, magnetic susceptibility and Mössbauer spectroscopy measurements in the series of composition $Fe_{1-x}Co_xSb_2O_4$ suggested the existence of some short range correlations within the chains [18, 19] whilst in materials of formulation Fe_1

$_{-x}Mg_xSb_2O_4$, the decrease in magnetic ordering temperature with increasing concentrations of magnesium was associated with non-magnetic Mg^{2+} ions weakening the magnetic interactions between Fe^{2+} ions [19, 20]. We have also demonstrated the capacity of these materials to accommodate additional oxygen within their structures [21].

Our previous work [3] reported on the reaction of $Mg_{0.50}Fe_{0.50}Sb_2O_4$ and $Co_{0.50}Fe_{0.50}Sb_2O_4$ with fluorine gas at low temperatures to give topotactic insertion of fluorine into the channels which are an inherent feature of the structure. Neutron powder diffraction and solid state NMR studies showed that the interstitial fluoride ions were bound to antimony within the channel walls to form $Sb-F-Sb$ bridges. ^{57}Fe Mössbauer spectra recorded at 300 K showed that oxidation of Fe^{2+} to Fe^{3+} was primarily responsible for balancing the increased negative charge associated with the presence of the fluoride ions within the channels.

In this work we report on the ^{57}Fe Mössbauer spectra recorded at low temperatures from new samples of the fluorinated phases of $Mg_{0.50}Fe_{0.50}Sb_2O_4$ and $Co_{0.50}Fe_{0.50}Sb_2O_4$ with the schafarzikite structure and their interpretation in terms of the number of near F^- ions which lie in the channels at the same value of the crystal z-coordinate as the iron ions and the magnetic properties of these materials.

2 Experimental

Materials of composition $Mg_{0.50}Fe_{0.50}Sb_2O_4$ and $Co_{0.50}Fe_{0.50}Sb_2O_4$ were prepared by heating appropriate quantities of the dried metal oxides in evacuated sealed quartz tubes as previously described [18, 20]. Fluorinated samples were obtained by heating the parent oxides in flowing fluorine gas (10% in nitrogen) at 230C and purging with gaseous nitrogen or argon [3]. The structural characterisation and analysis of the samples of composition $Fe_{0.5}Co_{0.5}Sb_2O_4F_{0.49}$ and $Fe_{0.5}Mg_{0.5}Sb_2O_4F_{0.31}$ has been reported previously [3]. In this work new samples were examined.

^{57}Fe Mössbauer spectra were recorded in a helium gas-flow cryostat in constant acceleration mode using a ca. 25 mCi ^{57}Co source. All spectra were computer fitted and all chemical isomer shift data are quoted relative to metallic iron at room temperature.

3 Results and discussion

3.1 $Co_{0.5}Fe_{0.5}Sb_2O_4F_x$

The ^{57}Fe Mössbauer spectra recorded at 298 K, 80 K, 45 K, 20 K and 5 K are shown in Fig. 2 and the fitting parameters are listed in Table 1. The spectra are different from those reported previously [3] which is not unexpected given that we have already noted [3] that differences in fluorine content probably relates to differences in particle size of starting materials and the fluorination conditions not being identical.

3.1.1 Formula of $Co_{0.5}Fe_{0.5}Sb_2O_4F_x$

Our initial analysis of the ^{57}Fe Mössbauer spectra was directed towards the evaluation of x and hence the formula of the material examined here. The spectrum recorded at 80 K shows the ratio of the combined Fe^{2+} components (with $\delta = 1.34 mms^{-1}$) to the Fe^{3+} component (with $\delta =$

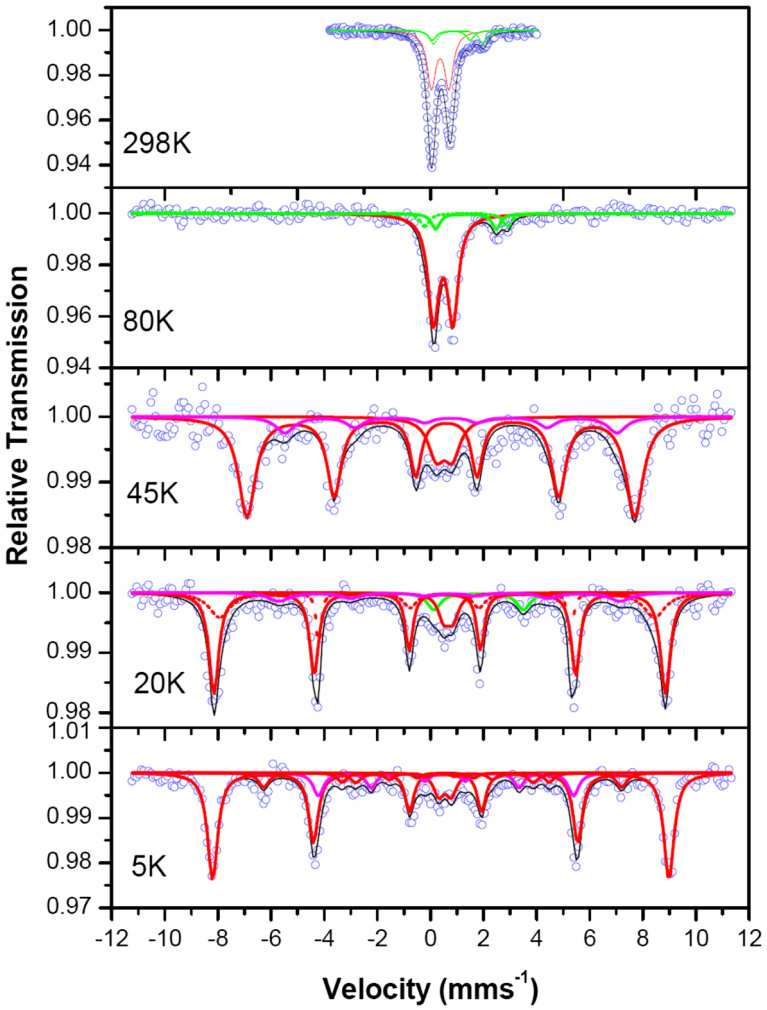

Fig. 2 ^{57}Fe Mössbauer spectra recorded from $Co_{0.5}Fe_{0.5}Sb_2O_4F_{0.41}$

0.48 mms^{-1}) to be 18: 82. Assuming charges of Co^{2+}, Sb^{3+}, and O^{2-} we calculate a value of x = 0.41 and hence a formula of $Co_{0.5}Fe_{0.5}Sb_2O_4F_{0.41}$.

3.1.2 Identification of components in spectra recorded at 298 K and 80 K

The spectrum recorded at 298 K showed a component with δ = 1.06 mms^{-1} which can readily be assigned to Fe^{2+} and components with δ = 0.41 mms^{-1} and δ = 0.37 mms^{-1} characteristic of Fe^{3+} (the partial superposition of the two components precludes their observation in Fig. 2). The small (ca. 7%) component with isomer shift δ = 0.79 mms^{-1} is intermediate between the isomer shift values for Fe^{2+} and Fe^{3+}. We assign this to an intermediate charge state related to some electron -delocalisation or -hopping of electrons between Fe^{2+} and Fe^{3+} ions. At 80 K and at lower temperatures this behaviour disappears as expected and the spectral components can be assigned as Fe^{2+} and Fe^{3+}.

Table 1 ^{57}Fe Mössbauer parameters recorded from $Co_{0.5}Fe_{0.5}Sb_2O_4F_{0.41}$

Temperature (K)	δ ± 0.02(mm s^{-1})	Δ or $e^2qQ/2$ ± 0.02(mm s^{-1})	H ± 0.5 (T)	LW ± 0.02 (mm s^{-1})	Area ± 5%
298	1.06	1.89	–	0.36	10
	0.79	1.44	–	0.38	7
	0.41	0.77	–	0.39	41
	0.37	0.66		0.39	42
80	1.34	3.12	–	0.39	8
	1.34	2.28		0.39	10
	0.48	0.73		0.48	82
45	0.50	−0.22	45.3	0.80	75
20	0.50	−0.20	52.8	0.50	60
5	0.50	−0.16	53.4	0.46	64

The fitting parameters listed in Table 1 show that in the spectrum recorded at 298 K the two Fe^{3+} components have slightly different values of quadrupole splitting. In the spectrum recorded at 80 K there are two Fe^{2+} components with slightly different values of quadrupole splitting. We have investigated whether this behaviour could be linked to different near neighbour fluoride configurations around the iron ions.

In the *ab* -planes containing the iron- and fluoride- ions the structure [3] shows that there are four possible sites for an inserted fluoride ion around each iron ion. A simulation incorporating random occupation by iron and cobalt of the cation sites and random occupation of surrounding fluoride sites (subject to their relative abundance, x) indicated that the relative percentages of an iron ion having 0,1,2,3 near neighbour fluoride ions was 9%, 42%, 42% and 7% respectively. This provides some indication that the observed difference in splitting in the doublets observed in spectra recorded in the paramagnetic regime corresponds to the main probabilities of having 1 or 2 fluoride neighbours.

3.1.3 Spectra recorded at 45 K, 20 K and 5 K

The spectra recorded below 80 K all show the superposition of magnetic sextet components. This is consistent with a magnetic ordering temperature $T_N = 75$ K recorded from magnetisation results recorded previously from the compound $Fe_{0.5}Co_{0.5}Sb_2O_4F_{0.49}$ [3]. Despite their complexity each spectrum is clearly dominated by a sextet of large spectral area with isomer shift characteristic of Fe^{3+}. We associate these sextet components as the low temperature versions of the large-area Fe^{3+}doublet components observed in the spectra recorded at 298 K and 80 K. In these sextet spectra the quadrupole shift Δ is evaluated from 2Δ = the energy difference between the splitting of lines 5 and 6 and lines 1 and 2 of the sextet. The angle Θ between the principal axis of the electric field gradient (EFG) and the direction of the magnetic hyperfine field B_{hf} can be evaluated from the values of Δ and the quadrupole splitting $e^2qQ/2$ observed in the 80 K spectrum using the relation

$$\Delta = e^2qQ/2.\tfrac{1}{2}.\left(3\cos^2\Theta - 1\right).$$

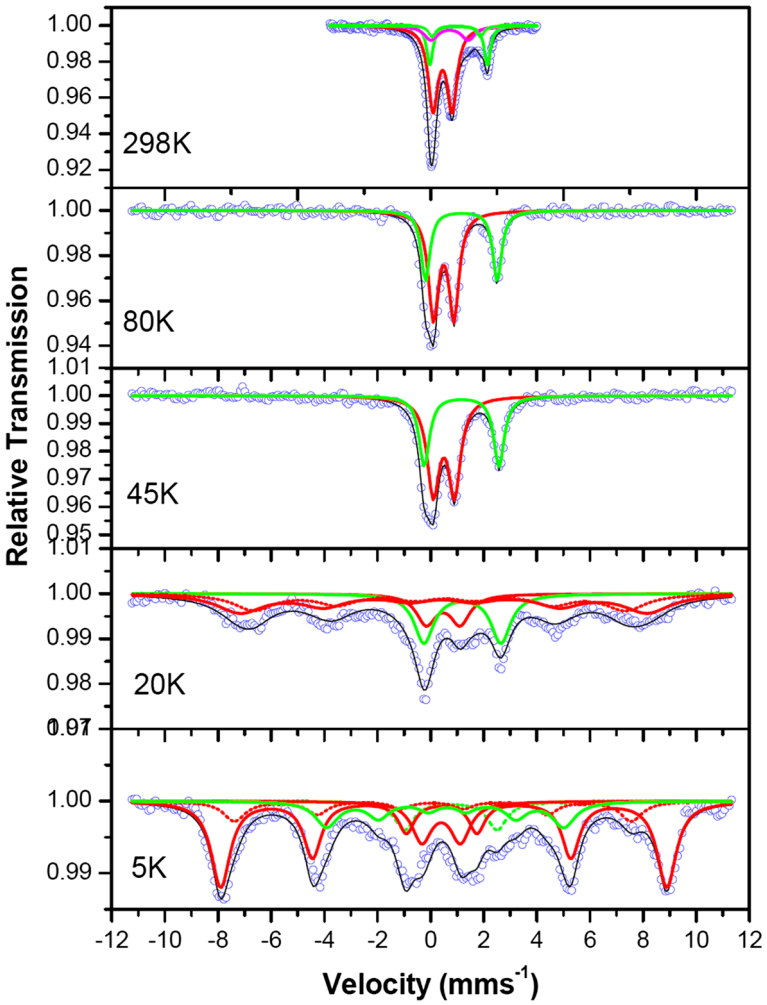

Fig. 3 ^{57}Fe Mössbauer spectra recorded from $Fe_{0.5}Mg_{0.5}Sb_2O_4F_{0.31}$

The values of Θ from the spectra at 45 K, 20 K and 5 K are evaluated as 69°, 67° and 64° respectively. These values are effectively identical to those measured in the parent material $FeSb_2O_4$ [10] and although there are differences – in $FeSb_2O_4$ the iron is Fe^{2+} and the magnetic structure is A- type instead of the present C- type – it seems that the insertion of fluoride ions into the channels of the structure does not affect the angle between EFG and magnetic hyperfine field. Given the complexity of the Fe^{2+} spectral components we have not analysed these to a degree which justifies inclusion of parameters in Table 1.

3.2 $Mg_{0.5}Fe_{0.5}Sb_2O_4F_x$

The ^{57}Fe Mössbauer spectra recorded at 298 K, 80 K, 45 K, 20 K and 5 K are shown in Fig. 3 and the fitting parameters are listed in Table 2.

Table 2 ^{57}Fe Mössbauer parameters recorded from $Fe_{0.5}Mg_{0.5}Sb_2O_4F_{0.31}$

Temperature (K)	δ ± 0.02(mm s^{-1})	Δ or $e^2qQ/2$ ± 0.02(mm s^{-1})	H ± 0.5 (T)	LW ± 0.02 (mm s^{-1})	Area ± 5%
298	1.05	2.17	–	0.29	20
	0.97	1.82	–	0.32	5
	0.71	1.40	–	0.63	15
	0.45	0.72		0.44	60
80	1.16	2.70	–	0.40	37
	0.49	0.77		0.46	63
45	1.17	2.81	–	0.48	39
	0.50	0.80	–	0.56	61
20	1.20	2.89	–	0.90	22
	0.46	0.04	47.6	2.10	37
	0.44	−0.10	43.5	1.80	28
5	0.46	0.04	52.1	0.90	49

3.2.1 Formula of $Mg_{0.5}Fe_{0.5}Sb_2O_4F_x$

The spectrum recorded at 80 K shows the ratio of the areas corresponding to the components assigned as Fe^{2+} and Fe^{3+} to be 37: 63. Application of the approach described in 3.1.1 above, and assuming the presence of Mg^{2+}, translates to a value of x = 0.31 and corresponds to a formula of $Mg_{0.5}Fe_{0.5}Sb_2O_4F_{0.31}$.

3.2.2 Identification of components

The spectra recorded at 80 K and 45 K are well fitted with a single Fe^{3+} quadrupole split component and a single Fe^{2+} quadrupole split component.

The spectrum recorded at 298 K spectrum shows- in addition to the Fe^{3+} and Fe^{2+} quadrupole split components- a component with isomer shift δ = 0.71 mms^{-1} which, as in $Co_{0.5}Fe_{0.5}Sb_2O_4F_{0.41}$, can be associated with electron mobility between Fe^{2+} and Fe^{3+} ions. At lower temperatures this component is not observed as electrons become localised on the Fe^{2+} and Fe^{3+} ions.

A simulation similar to that described in 3.1.2 above was performed – with x = 0.31. This indicated that the percentages of iron ions having 0,1 and 2 near neighbour fluoride ions is 25%, 50%, 25%. This distribution appears not to cause observable differences in quadrupole splitting for the Fe^{3+} components in the 298 K, 80 K and 45 K spectra or for the Fe^{2+} components in the 80 K and 45 K spectra.

3.2.3 Spectra at 20 K and 5 K

The spectra at 20 K and 5 K both show components representing magnetically ordered and non-ordered states of Fe^{2+} and Fe^{3+}ions. However, these components are not sufficiently well defined to enable the evaluation of the angle theta or further analysis. In particular the complexity of the Fe^{2+} spectral components precluded confident evaluation of parameters for inclusion in Table 2.

4 Conclusion

The ^{57}Fe Mössbauer spectra recorded from fluorinated $Mg_{0.50}Fe_{0.50}Sb_2O_4$ and $Co_{0.50}Fe_{0.50}Sb_2O_4$ show that a major effect of fluoride ion insertion involves the oxidation of

Fe^{2+} ions to Fe^{3+} ions in the structure. The ^{57}Fe Mössbauer spectra enable the degree of fluorination to be evaluated and the compositions to be derived. We suggest that that the multiplicity of components in the spectra recorded in the paramagnetic regime may be related to the number of near fluoride ions which lie in the channels at the same value of the crystal *z*-coordinate as the iron ions. Comparison of the magnetically ordered spectra recorded at lower temperatures from $Co_{0.5}Fe_{0.5}Sb_2O_4F_{0.41}$ with those recorded previously from $FeSb_2O_4$ indicates that the insertion of fluoride into the channels of the structure does not affect the angle between EFG and magnetic hyperfine field.

Acknowledgments We thank the Engineering and Science Research Council for financial support of this research (EPSRC EP/L014114/1).

References

1. Chevalier, B., Tressaud, A., Lepine, B., Amine, K., Dance, J.M., Lozano, L., Hickey, E., Etourneau, J.: Stabilization of a new superconducting phase by low temperature fluorination of La_2CuO_4. Physica C. **167**, 97–101 (1990)
2. Slater, P.R., Driscoll, L.: Photonic and Electronic Properties of Fluoride Materials. In: Tressaud, A. (ed.) Poppelmeier, Progress in Fluorine Science Series Vol 1, pp. 401–421. Elsevier, Amsterdam (2016) Modification of Magnetic and Electronic Properties, in Particular Superconductivity, by Low Temperature Insertion of Fluorine into Oxides
3. De Laune, B.P., Rees, G.J., Marco, J., Hah, H.-Y., Johnson, C.E., Johnson, J.A., Berry, F.J., Hanna, J.V., Greaves, C.: Topotactic Fluorine Insertion into the Channels of $FeSb_2O_4$-Related Materials. Inorg. Chem. **56**, 10078–10089 (2017)
4. Gavarri, J.R., Vigouroux, J.P., Calvarin, G., Hewat, A.W.: Structure de $SnPb_2O_4$ à quatre températures: relation entre dilatation et agitation thermiques. J. Solid State Chem. **36**, 81–90 (1981)
5. Fischer, R., Pertlik, F.: Tschermaks Miner. Petrogr. Mitt. **22**, 236–241 (1975)
6. Gonzalo, J.A., Cox, D.E., Shirane, G.: The Magnetic Structure of $FeSb_2O_4$. Phys. Rev. **147**, 415–418 (1966)
7. Chater, R., Gavarri, J.R., Hewat, A.W.: Structures isomorphes MeX2O4—Evolution structurale entre 2 K et 300 K de l'antimonite $FeSb_2O_4$: Elasticité et ordre magnétique anisotropes. J. Solid State Chem. **60**, 78–86 (1985)
8. Varret, F., Imbert, P., Gerard, A., Hartmann-Boutron, F.: Etude de $FeSb_2O_4$ par effet Mössbauer. Solid State Commun. **6**, 889–892 (1968)
9. Pettit, G., Meder, M.R.: ^{57} Fe Mossbauer spectra from $FeSb_2O_4$ Hyperfine Interact. **5**, 323 (1978)
10. Bayliss, R.D., Berry, F.J., de Laune, B.P., Greaves, C., Helgason, O., Marco, J.F., Thomas, M.F., Vergara, L., Whitaker, M.J.: Magnetic interactions in ferrous antimonite, $FeSb_2O_4$, and some derivatives J. Phys. Condens. Matter. **24**, 276001 (2012)
11. Eibschutz, M., Ganiel, U.: Mössbauer studies of paramagnetic $FeSb_2O_4$. Solid State Commun. **6**, 775–777 (1968)
12. Tammann, G.: Chemische Reaktionen in pulverförmigen Gemengen zweier Kristallarten. Z. Anorg. Allg. Chem. **149**, 21–34 (1925)
13. Koyama, E., Nakai, I., Nagashima, K.: Hydrothermal synthesis of a single crystal of $FeSb_2O_4$ and isostructural compounds Nippon Kagaku Kaishi. **6**, 793–795 (1979)
14. Gavarri, J.R., Calvarin, G., Chardon, B.: Composés isomorphes MeX2O4: Dilatation thermique anisotrope et ordre magnétique dans $MnSb_2O_4$. J. Solid State Chem. **47**, 132–142 (1983)
15. Witteveen, H.T.: Magnetic susceptibility of $NiAs_2O_4$ and $NiSb_2O_4$ Solid State Commun. **9**, 1313–1315 (1971)
16. Ståhl, S.: The crystal structure of $ZnSb_2O_4$ and isomorphous compounds Ark. Khem. Min. Geol. **17B**, 1–7 (1943)

17. Atanasova, M.T., Strydom, A.M., Schutte, C.J..H., Prinsloo, L.C., Focke, W.W.: Crystal structure and magnetic properties of $CuSb_2O_4$. J. Mater. Sci. **49**, 3497–3510 (2014)
18. Cumby, J., de Laune, B.P., Greaves, C.: The structures and magnetic properties of $Fe_xCo_{1-x}Sb_2O_4$ and $Mn_xCo_{1-x}Sb_2O_4$ J. Mater. Chem. C. **4**, 201–208 (2016)
19. Berry, F.J., de Laune, B.P., Greaves, C., Hah, H.-Y., Johnson, C., Johnson, J.A., Kameli, S., Whitaker, M.J., Marco, J.F., Thomas, M.F., Whitaker, M.J.: Magnetic interactions in $Fe_{1-x}M_xSb_2O_4$ (M=Mg,Co) deduced from Mossbauer spectroscopy Hyperfine Interact. **239**, 31–39 (2018)
20. de Laune, B.P., Whitaker, M.J., Marco, J.F., Thomas, M.F., Berry, F.J., Lees, M.R., Greaves, C.: Synthesis and magnetic characterization of $Fe_{1-x}Mg_xSb_2O_4$ (x=0.25, 0.50, 0.75) and their oxygen-excess derivatives J. Mater. Chem. C. **5**, 4985 (2017)
21. de Laune, B.P., Rees, G.J., Whitaker, M.J., Hah, H.-Y., Johnson, C., Johnson, J.A., Brown, D.E., Tucker, M.G., Hansen, T.C., Berry, F.J., Hanna, J.V., Greaves, C.: Oxygen insertion reactions within the 1-D channels of phases related to $FeSb_2O_4$ Inorg. Chem. **56**, 594 (2017)